

OXIDATIVE DEGRADATION OF ORGANIC ACIDS IN FGD PROCESS

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ABSTRACT

Organic acid degradation coupled with sulfite oxidation has been studied under flue gas desulfurization (FGD) conditions. The ratio of the reaction rate constants (degradation to oxidation) was used to characterize the degradation behavior of organic acids. The ratio was shown to be independent of pH, dissolved oxygen, and dissolved sulfite/bisulfite. However, this ratio was increased by certain transition metal ions such as Co, Ni, and Fe, and was decreased by Mn and halides. Hydroxyl and sulfonated carboxylic acids degraded approximately three times slower than saturated dicarboxylic acids, while unsaturated dicarboxylic acids degraded an order of magnitude faster. A wide spectrum of dicarboxylic acid degradation products were found, including carbon dioxide, hydrocarbons, lower molecular weight mono- and dicarboxylic acids, and other carbonyl compounds.

INTRODUCTION

Currently, limestone scrubbing is the dominant commercial technology for flue gas desulfurization (FGD) (1). The performance of limestone scrubbing is chemically limited by two pH extremes: (a) low pH near the gas/liquid interface which decreases the SO_2 solubility and absorption rate; and (b) high pH near the liquid/solid interface which decreases the limestone solubility and dissolution rate (2, 3). Organic acids that buffer between pH 3.0 and pH 5.5 enhanced SO_2 removal efficiency and limestone utilization at concentrations of 5 to 10 mM (2-10).

Adipic acid was the first buffer successfully and generally applied to the FGD process (3, 9, 11, 12). It has been replaced commercially by dibasic waste acid (DBA), a waste from adipic acid and cyclohexanone production, containing primarily adipic, glutaric, and succinic acids. The effectiveness of DBA is equivalent to adipic acid (3, 9). Other potential alternatives include hydroxycarboxylic acids and sulfonated carboxylic acids (10, 13, 14). They are of interest because of reduced volatility and potentially lower degradation rates.

In addition to the expected loss of organic acid additive by entrainment of solution in waste solids, chemical degradation (15) and coprecipitation (16) losses are also observed. Chemical degradation, which is conjugated with sulfite oxidation (15), is the most important mechanism of buffer loss under forced oxidation conditions (3, 9).

A rate expression for adipic acid degradation under scrubber conditions was derived by Rochelle (15). Assuming that both sulfite oxidation (17) and organic acid degradation (18) are free radical reactions proceeding by a common radical, R^\bullet :

$$d[A]/dt = k_1 [A] [\text{R}^\bullet] \quad (1)$$

$$d[\text{S(IV)}]_d/dt = k_2 [\text{S(IV)}]_d [\text{R}^\bullet] \quad (2)$$

where, A and S(IV) stand for organic acid, sulfite/bisulfite and the subscripts d and t denote 'dissolved' and 'total' respectively, then the rate of degradation is given by

$$d[A]/dt = k_{12} ([A]/[\text{S(IV)}]_d) (d[\text{S(IV)}]_d/dt) \quad (3)$$

where $k_{12} \equiv k_1/k_2$. Previous works have correlated rates by the degradation rate constant k_d , defined as $k_{12}/[\text{S(IV)}]_d$. The most probable free radical here is $\text{SO}_4^{\bullet-}$, because of its reactivity toward alcohols which are inhibitors of sulfite oxidation (19) and because it has been cited as the active species in the decarboxylation/oxidation of organic acids by persulfate (S_2O_8) (20, 21).

Valeric acid, glutaric acid, and hydrocarbons from ethane to butane were identified as degradation products of adipic acid (15, 16). Low pH, especially in the presence of manganese reduced the degradation of adipic acid (22). It was also found that high dissolved S(IV) reduced the degradation (23).

It is desirable to understand the degradation kinetics, the mechanism, and the additional environmental impact caused by degradation. This paper covers the degradation kinetics and products. Since decarboxylation is the major degradation pathway, and it is decarboxylation that significantly affects the buffering capacity, CO_2 evolution rate instead of the actual degradation rate is of greater interest. Furthermore, k_{12} , the ratio of k_1 to k_2 instead of k_d , will be used for most kinetic studies, since this ratio excludes the effect of $[\text{S(IV)}]_d$.

EXPERIMENTAL

The reactor used for this study was a closed system, semibatch reactor (continuous to gas but batch to solution or slurry). Figure 1 gives the block diagram of the experimental apparatus.

In a typical experiment, 1.0 M synthesized CaSO_4 solids were slurried and oxidized in a solution containing 10 mM organic acid and 0.1 M $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ seed crystals. All experiments were performed at a constant temperature of 55°C. pH was maintained constant throughout a given experiment.

Total S(IV) was analyzed by iodometric titration of the slurry sample. Filtered samples were reheated to 55°C, the experimental temperature, and the pH was adjusted back to the original pH (4.5 - 5.5±0.01) with sodium sulfite or air oxidation. Then iodometric titration was applied to measure the dissolved S(IV). CO_2 was monitored continuously by an infrared CO_2 detector. Hydrocarbons, organic acids and liquid degradation products were analyzed by ion chromatograph exclusion (ICE, Dionex 14), gas chromatography (GC, Varian 3700), and/or gas chromatograph - mass spectrometer (GC/MS, Finnigan 4023). More detailed procedures and conditions are available elsewhere (10).

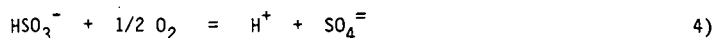
For better control of dissolved S(IV), some experiments were run with sodium sulfite solution in the presence of 10 mM organic acid and 0.3 M sodium sulfate to prevent any dramatic change in ionic strength. Only the CO_2 evolution rate was measured. The oxidation rate was fixed by the sodium sulfite titration rate. k_d and k_{12} were then calculated according to Equation 3.

RESULTS AND DISCUSSIONS

Most of the experiments were performed with adipic acid or glutaric acid. It was found that these acids degraded at practically identical rates and that the molar rate of CO_2 evolution was equal to the molar rate of degradation at the initial stage.

Sulfite Oxidation Rate - The effect of the sulfite oxidation rate on adipic acid degradation was studied in sodium sulfite solution system at pH 5.0, without addition of metal ions. When the oxidation rate, controlled by the sodium sulfite feedrate, increased from 0.0082 to 0.024 M/hr, $[\text{S(IV)}]_d$ changed from 0.74 to 1.2 mM, and the carbon dioxide evolution rate changed from 0.13 to 0.20 mM/hr. Accordingly, k_d changed from 1.58 to 0.82 M^{-1} , while k_{12} only changed from 1.17×10^{-3} to 0.99×10^{-3} . Therefore, the organic acid degradation rate is directly proportional to the sulfite oxidation rate.

pH and Dissolved S(IV) - It was generally observed that little organic acid degradation occurred in the calcium sulfite slurry system at low pH (22). However, dissolved S(IV) is significantly affected by pH in this system (Table 1). Therefore, sodium sulfite solution at pH 5.0 was used for better control of dissolved S(IV). The dissolved S(IV) variation caused by oxidation was reflected by pH change:



Therefore, the addition of sodium sulfite to maintain constant pH would keep dissolved S(IV) constant. The same approach has been used for the studies of limestone dissolution (24), sulfite oxidation (17, 25), and calcium sulfite dissolution/crystallization (26). The experimental data followed the rate expression nicely, and k_{12} was found to be inversely proportional to $[S(IV)]_d$ without addition of metal ions (Figure 2). In other words, as predicted, k_{12} was independent of $[S(IV)]_d$ which itself was a strong function of pH in calcium sulfite slurry. Further studies confirmed the null effect of pH on k_{12} (Figure 3). Therefore, it was very clear that in calcium sulfite slurry, it was $[S(IV)]_d$, not pH, that significantly controlled organic acid degradation rate. Figure 3 also indicates that k_{12} declines, in the presence of 0.1 mM Fe, as the pH increases over 5.0. Also different values of k_{12} are obtained for different catalyst conditions. These catalyst effects will be discussed later in the section on transition metals.

Oxygen - The sulfite oxidation rate can be expressed in terms of the oxygen absorption rate as :

$$R = k'(P_{O_2}^* - P_{O_2}) \quad (5)$$

where $P_{O_2}^*$ and P_{O_2} are vapor pressures corresponding to the saturation and bulk concentration, respectively. Experimentally, $P_{O_2}^*$ was controlled by mixing oxygen and nitrogen. The experiments shown in Figure 4 were performed with very low oxidation rate. Therefore, the solution was practically saturated to O_2 at the partial pressure in the feed gas. Figure 4 shows that k_{12} is independent of P_{O_2} . Again, k_{12} values were different for different catalyst conditions.

Transition Metals - It was shown above that k_{12} is a strong function of catalyst environment. Among the transition metals, Mn and Fe are of greater interest because of their presence in the scrubbing system. Both Mn and Fe are effective catalysts for sulfite oxidation (17), and are predicted theoretically to catalyze oxidation with 0.5 power (19, 27, 28). It was observed that organic acid degradation was increased by Fe but decreased by Mn. Probably the degradation rate varied with Fe and Mn to the first and zero order, respectively. If this hypothesis is correct, k_{12} should vary with Fe to the 0.5 power and with Mn to the -0.5 power. The solubility of ferrous sulfate was limited by pH (Table 1). This limitation justifies the declining k_{12} in Figure 3. Slurry experiments using iron-free synthesized calcium sulfite solids with known amounts of added ferrous sulfate within its solubility showed that the adipic acid degradation rate constant, k_d , varied with dissolved iron to the power of 0.6 (Figure 5). However, slurry experiments with varying Mn were less quantitative but demonstrated reduced k_{12} at higher Mn (Figure 6).

The first series of transition metals except Sc and Zn were studied in sodium sulfite clear solution system. All of these transition metals except Ti and Cr, caused an increment of k_{12} (Table 2). Titanium dioxide might have a solubility problem, and chromium sulfate might interfere dissolved S(IV) measurement.

Mn is capable of two-electron transfer. Thallium (Tl), another transition metal able to transfer two electrons, was studied in calcium sulfite slurry because of the interference with dissolved S(IV) measurement. With the addition of 1 mM Tl, k_d decreased from 1.5 and 2.5 to 0.6 and 0.7 M^{-1} for pH 5.0 and pH 5.5, respectively. The mechanism is still unclear. But there is a trend that transition metals transferring one electron increase degradation while transition metals transferring two electrons decrease degradation.

Halides - It has been reported that decomposition of carboxylate salts during sulfite oxidation is suppressed by the presence of 2 to 10% by weight of chloride ion in the aqueous absorbent (29). Table 3 lists the resulting k_{12} values of adipic acid with different concentration of chloride, bromide, and iodide. Manganese effects are included for the convenience of comparison. In clear sodium sulfite solution system, chloride reduces k_{12} significantly only when its concentration is as high as 100 mM. On the other hand, the iodide effect is so strong that even in the presence of 0.1 mM Fe, 0.1 mM iodide reduces k_{12} to 0.1×10^{-3} . The corresponding value for Mn in the

absence of Fe is approximately 0.7×10^{-3} . Bromide behaves moderately. Its effect is between chloride and iodide.

Alternatives - The potential buffer additives covered here can be grouped into dicarboxylic (adipic, glutaric), hydroxycarboxylic (4-hydroxycarboxylic), sulfonated carboxylic (sulfosuccinic), and unsaturated carboxylic (maleic) acids. Sulfosuccinic acid is not commercially available, but can be easily synthesized by reaction of maleic acid with sodium sulfite (10, 30)

k_{12} is found to be a strong function of functional group (Table 4). Unsaturated maleic acid degrades about seven times faster than dicarboxylic acids, probably due to the presence of conjugated double bonds. In reducing the degradation of maleic acid, Mn is not as effective as in the case of dicarboxylic acids. Fe is inert to maleic acid degradation. On the other hand, 4-hydroxybutyric acid degrades about three times slower than dicarboxylic acids probably due to the formation of an intramolecular hydrogen bond. Sulfosuccinic acid behaves more or less in the same way as 4-hydroxybutyric acid except that Fe has no significant effect on the degradation of sulfosuccinic acid.

Degradation Products - The degradation products of adipic acid are widely distributed. They can be classified as dicarboxylic acids, monocarboxylic acids, hydroxycarboxylic acids, keto-acids, furans, hydrocarbons, and carbon dioxide (Table 5). The degradation product distribution is also a strong function of catalyst environment. In the presence of 1 mM Mn, glutaric and valeric acids are the major products except for carbon dioxide which is the primary degradation product for all cases. In the absence of Mn, 4-formylbutyric acid is the major liquid phase product. Although oxygen would be required to generate a smaller dicarboxylic acid, the dissolved oxygen in the presence of 1 mM Mn should be practically zero because of the mass transfer-controlled sulfite oxidation. Probably, Mn is an effective carrier of oxygen to the degradation product(s).

DISCUSSIONS

The proposed rate expression for organic acid degradation is very useful for comparing the degradation behavior of different organic acids. The degradation of organic acid is directly proportional to its concentration, to the sulfite oxidation rate and inversely to the concentration of dissolved sulfite/bisulfite. However, the rate expression needs modification under different catalyst environment. In general, sulfonated organic acids and hydroxycarboxylic acids degrade much slower than adipic or glutaric acids, while unsaturated carboxylic acids, especially with conjugated double bonds degrade much faster.

In summary, the degradation rate constant ratio, k_{12} , is independent of dissolved sulfite/bisulfite, dissolved oxygen or pH. However, it is reduced by transition metals with two-electron transferred capability, such as Mn and Ti. It is also inhibited by halides. Mn is very effective in reducing k_{12} . Iodide is even more efficient in inhibiting degradation. On the other hand, k_{12} is enhanced by one electron-transferred transition metals, especially by Fe. It should be emphasized that pH affects the solubility of iron and calcium sulfite, which both affect the degradation. However, the effects of iron solubility and dissolved S(IV) are opposite on organic acid degradation. Therefore, low pH will not necessarily reduce organic acid degradation, even in the calcium sulfite slurry system.

The degradation product pattern of adipic acid is a strong function of catalyst environment. Manganese gives glutaric and valeric acids as the major liquid phase products, while 4-formylbutyric acid is the major corresponding product in the absence of manganese. Carbon dioxide is the major degradation product in all cases. In addition, other mono- and dicarboxylic acids, hydrocarbons, hydroxycarboxylic acids and other carbonyl compounds such as 4-oxopentanoic acid are observed as degradation products of adipic acid.

Table 1 The Effects of pH and Sulfite Oxidation Rate on the Solubility of MnSO_4 , FeSO_4 , and $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$

| pH | $\text{Fe}^a(\text{mM})$ | | $\text{Mn}^b(\text{mM})$ | | $[\text{S(IV)}]_d(\text{mM})$ | |
|-----|--------------------------|------------------|--------------------------|------------------|-------------------------------|------------------|
| | $\text{Rox}^c=0$ | $\text{Rox}=0.5$ | $\text{Rox}=0$ | $\text{Rox}=0.5$ | $\text{Rox}=0$ | $\text{Rox}=0.5$ |
| 4.0 | 0.15 | 0.13 | 0.43 | 0.43 | 34.2 | 27.0 |
| 4.5 | 0.12 | 0.12 | 0.45 | 0.46 | 24.8 | 14.5 |
| 5.0 | 0.02 | 0.02 | 0.46 | 0.46 | 9.3 | 5.9 |
| 5.5 | ≤ 0.01 | ≤ 0.01 | 0.47 | 0.46 | 3.9 | 1.3 |

a 0.1 mM was added

b 0.5 mM was added

c Rox = sulfite oxidation rate (M/hr)

Table 2 Effects of Transition Metals on k_{12} in Sodium Sulfite Solution by CO_2 Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

| Conc (mM) | Degradation to Oxidation Constant Ratio, $k_{12} \times 10^3$ | | | | | |
|-----------------|---|------|------|------|---------|-------|
| | Co | Ni | Cu | Ti | V | Cr |
| 0 | 0.81 | 0.89 | 0.87 | 0.86 | 1.10 | 0.99 |
| 0.03 | 0.84 | - | 0.89 | - | - | - |
| 0.1 | 0.76 | 1.18 | 0.93 | - | 1.23 | 1.03 |
| 0.3 | 0.82 | - | 1.00 | 0.90 | 1.43 | 1.02 |
| 1.0 | 0.99 | 2.48 | 1.31 | 0.86 | 1.46 | 1.02 |
| 3.0 | 1.60 | - | 1.33 | 0.84 | 1.54 | - |
| 10.0 | 3.30 | - | - | - | - | - |
| oxidation state | 2,3 | 2,3 | 1,2 | 3,4 | 2,3,4,5 | 2,3,6 |

Table 3 Effects of Halide on k_{12} in Sodium Sulfite Solution by CO_2 Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

| Conc.(mM) | Degradation to Oxidation Constant Ratio, $k_{12} \times 10^3$ | | | |
|-----------|---|------|-----|-----------------|
| | KCl | KBr* | KI* | MnSO_4 |
| 0 | 1.0 | 2.7 | 3.1 | 1.0 |
| 0.1 | - | 2.3 | 0.1 | 0.7 |
| 0.3 | - | 2.0 | - | 0.3 |
| 1 | - | 1.5 | - | 0.3 |
| 10 | - | 0.2 | - | - |
| 30 | 0.8 | - | - | - |
| 100 | 0.6 | - | - | - |
| 300 | 0.3 | - | - | - |

* with 1.0 mM Fe

Table 4 Comparison of Organic Acids as Buffer Additives in Terms of k_{12}
at pH 5.0, 55°C, in Sodium Sulfite Solution by CO₂ Evolution

| Organic Acid | Degradation to Oxidation Rate Constant Ratio, $k_{12} \times 10^3$ | | |
|------------------|--|-------------|----------------|
| | with 1 mM Mn | No Catalyst | with 0.1 mM Fe |
| Adipic | 0.3 | 1.0 | 3.0 |
| Glutaric | 0.3 | 1.0 | 3.0 |
| 4-Hydroxybutyric | 0.1 | --- | 1.4 |
| Sulfosuccinic | 0.1 | 0.3 | 0.3 |
| Maleic | 3.6 | 6.7 | 7.0 |

Table 5 Degradation Products from 80% Degradation of 10 mM Adipic Acid
in Calcium Sulfite Slurry with 0.1 mM Mn at pH 5.0, 55°C
in Terms of the Percentage of the Initial Concentration (mM C)

| Dicarboxylic | Monocarboxylic | Hydroxycarboxylic | Hydrocarbons | Others |
|----------------------|------------------|---------------------------|-----------------|---|
| C6 Adipic (20) | | | | Tetrahydro-2,5-furan Dicarboxylic(*) |
| C5 Glutaric (1.5) | Valeric (0.7) | 5-Hydroxyvaleric (2.5) | | 4-Formylbutyric (6.7) 4-Oxopentanoic (0.3) |
| C4 Succinic (0.1) | Butyric (0.4) | 4-Hydroxybutyric (2.5) | Butane (1.0) | 3-Formylpropionic (*) Furane (0.6) |
| C3 Malonic (2.3) | -- | | Propane (*) | |
| C2 | -- | | Ethane (*) | |
| C1 | Formic (2.0) | | Methane (*) | Formaldehyde (*) CO ₂ (49) |

* less than 0.1%

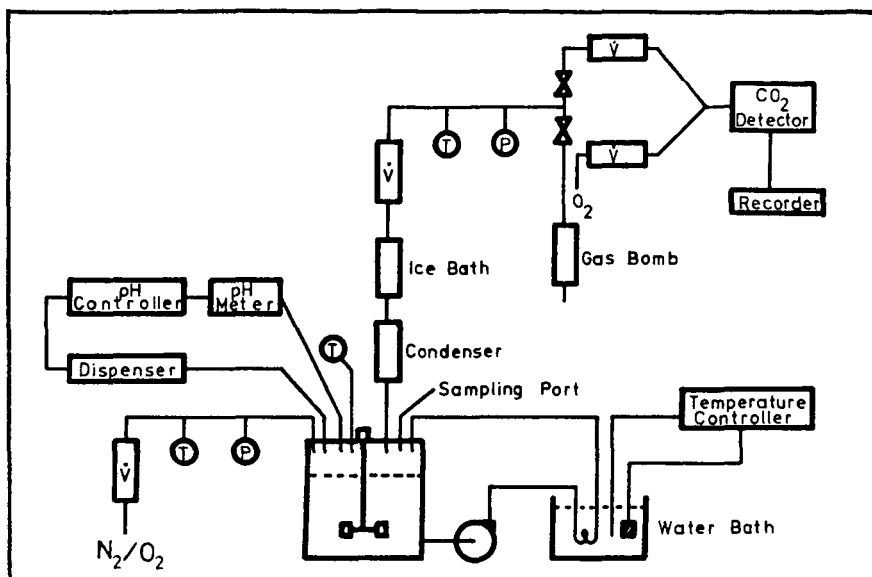


Figure 1 The Apparatus for Oxidative Degradation of Organic Acids

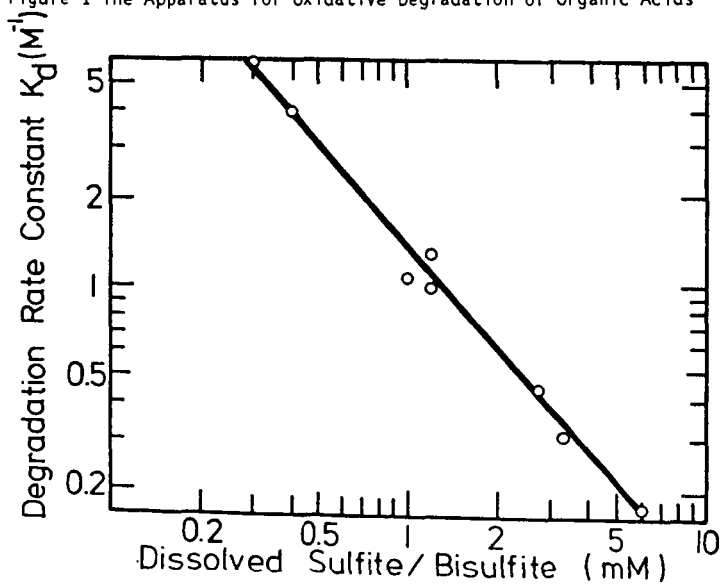


Figure 2 The Effects of Dissolved Sulfite/Bisulfite on k_d in Sodium Sulfite Solution at pH 5.0, 55°C, by CO_2 Evolution

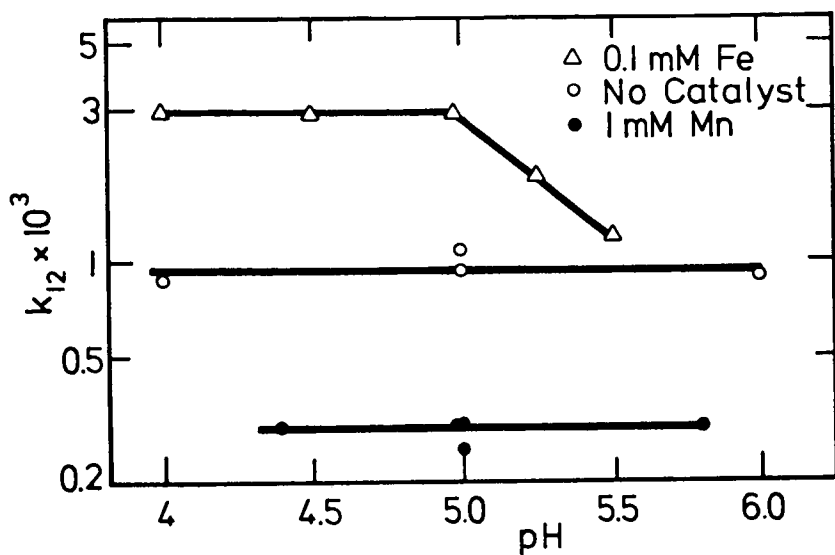


Figure 3 The Effect of pH on k_{12} in Sodium Sulfite Solution at pH 5.0, 55°C by CO_2 Evolution

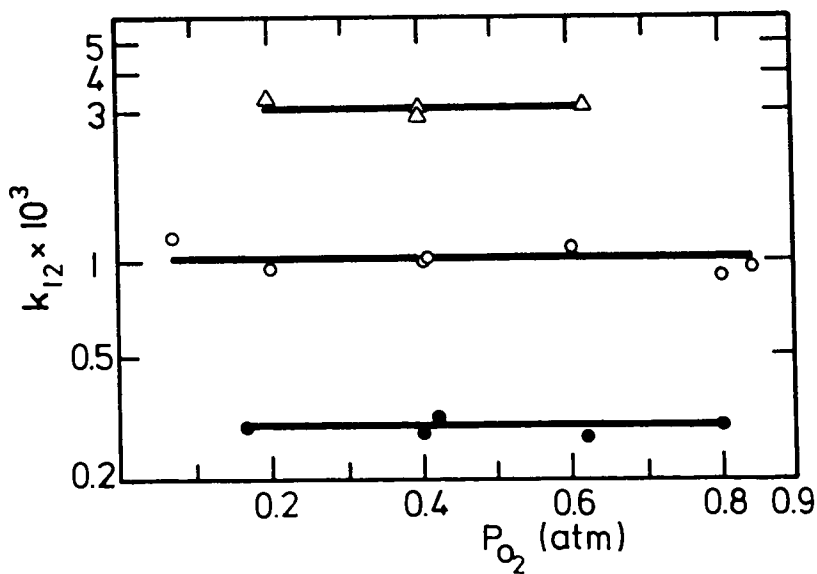


Figure 4 The Effect of Oxygen Vapor Pressor on k_{12} in Sodium Sulfite Solution at pH 5.0, 55°C by CO_2 Evolution

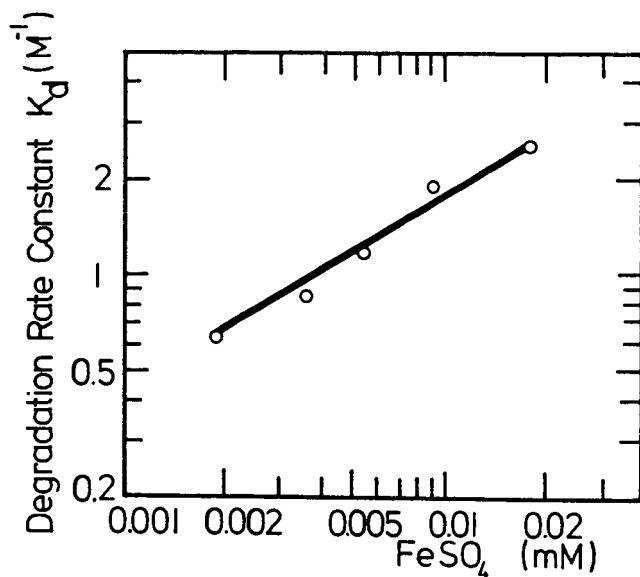


Figure 5 The Effect of Iron on k_d in Calcium Sulfite Slurry at pH 5.0, 55°C by CO₂ Evolution

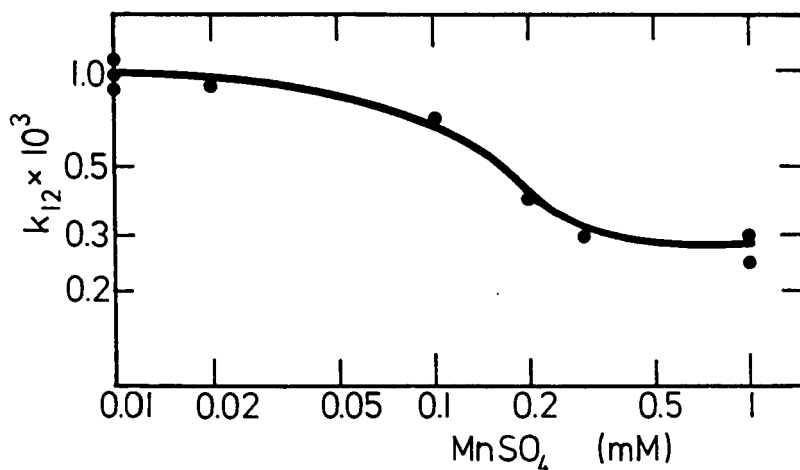


Figure 6 The Effect of Manganese on k_{12} in Calcium Sulfite Slurry at pH 5.0, 55°C by CO₂ Evolution

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